13a

(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. AU 199948956 B2
(10) Patent No. 753298

(54) Title
Effect pigments coated with reactive orientation auxiliary agents

(51)6 International Patent Classification(s)
C09C 003/08 C09C 003/12
C09C 003/10

(21) Application No: 199948956 (22) Application Date: 1999.05.03

(87) WIPO No: WO99/57204

(30) Priority Data

| (31) Number | (32) Date | (33) Country |
|---|---|---|
| 19820112 | 1998.05.06 | DE |

(43) Publication Date : 1999.11.23
(43) Publication Journal Date : 2000.02.03
(44) Accepted Journal Date : 2002.10.17

(71) Applicant(s)
Eckart-Werke Standard Bronzepulver-Werke Carl-Eckart GmbH and Co.

(72) Inventor(s)
Klaus Greive; Alfried Kiebl

(74) Agent/Attorney
F B RICE and CO,605 Darling Street,BALMAIN NSW 2041

(56) Related Art
EP 634459

48956/99

**PCT** WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro
INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation 6 : C09C 3/08, 3/10, 3/12

A1

(11) Internationale Veröffentlichungsnummer: WO 99/57204

(43) Internationales Veröffentlichungsdatum: 11. November 1999 (11.11.99)

(21) Internationales Aktenzeichen: PCT/DE99/01333

(22) Internationales Anmeldedatum: 3. Mai 1999 (03.05.99)

(30) Prioritätsdaten:
198 20 112.5 6. Mai 1998 (06.05.98) DE

(71) Anmelder *(für alle Bestimmungsstaaten ausser US)*: ECKART-WERKE STANDARD BRONZEPULVER-WERKE CARL-ECKART GMBH & CO. [DE/DE]; Kaiserstrasse 30, D-90763 Fürth (DE).

(72) Erfinder; und

(75) Erfinder/Anmelder *(nur für US)*: GREIWE, Klaus [DE/DE]; Erlenstrasse 6, D-91207 Lauf (DE). KIEHL, Alfried [DE/DE]; Blütenstrasse 5, D-91220 Schnaittach (DE).

(74) Anwalt: PÖHLAU, Claus; Louis, Pöhlau, Lohrentz & Segeth, Postfach 30 55, D-90014 Nürnberg (DE).

(81) Bestimmungsstaaten: AU, CA, JP, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

**Veröffentlicht**
*Mit internationalem Recherchenbericht.*
*Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.*

(54) Title: EFFECT PIGMENTS COATED WITH REACTIVE ORIENTATION AUXILIARY AGENTS

(54) Bezeichnung: MIT REAKTIVEN ORIENTIERUNGSHILFSMITTELN BESCHICHTETE EFFEKTPIGMENTE

(57) Abstract

The invention relates to an effect pigment coated with surface modifying agents in which the starting pigment comprises a layer having at least one reactive surface modifying agent. The surface modifying agent is a compound which is chemically bound to the initial pigment by at least two functional groups which are different from one another and which are separated by a spacer. The invention also relates to a method for producing such an effect pigment.

(57) Zusammenfassung

Gegenstand der Erfindung ist ein mit Oberflächenmodifizierungsmiteln beschichtetes Effektpigment, bei dem das Ausgangspigment eine Schicht mit wenigstens einem reaktiven Oberflächenmodifizierungsmittel aufweist, wobei das Oberflächenmodifizierungsmittel eine Verbindung ist, die wenigstens zwei voneinander verschiedene und durch einen Spacer beabstandete funktionelle Gruppe chemisch an das Ausgangspigment gebunden ist. Ferner wird ein Verfahren zur Herstellung eines derartigen Effektpigments angegeben.

## Abstract

The subject of the invention is an effect pigment which is coated with surface-modifying agents, wherein the initial pigment has a layer with at least one reactive surface-modifying agent, wherein the surface-modifying agent is a compound which has at least two functional groups which are different from each other and which are spaced by a spacer, chemically bound to the initial pigment. Also described is a process for the production of an effect pigment of that kind.

# Effect pigments coated with reactive orientation aids

The present invention concerns effect or fancy pigments whose ~~surface~~ is modified with orientation aids.

The literature (EP 0 634 459 A2) describes coating pearl shine pigments with alkyl silanes to improve orientation of the pigments in the ambient medium (paint or lacquer, casting resin etc). The modification process used in that case controls the wetting characteristics of the pearl shine pigments by the introduction of hydrophobing alkyl silanes and results in a leafing effect, as is also known in relation to metal effect pigments.

The application of stearic acid to the pigment surface means that aluminium pigments can also be strongly hydrophobed, which then results in poorer wetting of the pigments by the individual components of the paint or lacquer. The content of the pigments is then increased at the interfaces (or the surface) of the liquid film of paint or lacquer. As after hardening of the film of paint or lacquer that results in coatings with a high level of brilliance, this is referred to as good orientation characteristics in respect of the pigments ('leafing effect'). The aluminium pigments which are oriented at the surface are however not particularly resistant to weathering as they are not enclosed in the film of paint or lacquer and thus protected from corrosion. In the case of metallic paints for automobiles, which must satisfy particularly high levels of weathering stability, therefore only aluminium pigments which are non-leafing (which can be well wetted) are used. Paints in the automobile sector involve a layer structure which in the case of metallic paints generally consists of five layers. Disposed on the metallic substrate is a phosphate layer, followed by a cathodic dip lacquering (CDL), a filler layer (to compensate for irregularities and unevenness etc), the base lacquer and finally the clear lacquer. The actual layer which affords the effect is the base lacquer which generally contains a mixture of metal pigments and pearl shine pigments and which nowadays is already used in many cases in the form of a water-based lacquer. The clear lacquer serves to protect the base lacquer and to 'smooth out' the surface.

Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed in Australia before the priority date of each claim of this application.

A preferred embodiment of the present invention provides effect pigments which on the one hand are easily wetted by the binding agent or solvent of the paint or lacquer and which can be well oriented in the liquid film of lacquer and which on the other hand involve an intimate bond with the surrounding binding agent matrix and therefore do not suffer from the above-described disadvantages involved in use thereof.

In one aspect, the present invention is directed towards an effect pigment coated with surface modifying agents, characterised in that the initial pigment has a layer comprising at least one reactive surface-modifying agent, wherein the surface-modifying agent is a compound which has at least two functional groups which are different from each other and which are spaced by a spacer and of which at least one functional group is chemically bound to the initial pigment.

In a preferred embodiment, the present invention is directed to an effect pigment coated with surface-modifying agents, characterised in that the initial pigment has a layer with at least one reactive surface-modifying agent, wherein the surface-modifying agent is a compound which has at least two terminal functional groups which are different from each other and which are spaced by a spacer comprising alkyl chains, silanes, siloxanes, polyethers, thioethers or unrethanes or combinations of those groupings having the general formula $(C,Si)_nH_m(N,O,S)_x$ with n = 0-50, m = 0-100 and x = 0-50, and of which at least one functional group is chemically bound to the initial pigment, and the effect pigment is further of a particle size of between 1 and 200 μm and exhibits the behaviour of a non-leafing pigment.

At least one functional group which is directed outwardly, that is to say towards the binding agent, of the effect pigment according to the invention can react chemically with the binding agent in that case in a kind of cross-linking reaction. By virtue of the resulting strongly covalent bonding forces at the pigment/binding agent interface, water vapour in the finished coating can only diffuse with difficulty into the pigmented binding agent matrix. The strong

linkage of the pigments to the binding agent of the base lacquer, which is caused by the relatively good wettability of the metal pigments coated with the reactive orientation agent means that there cannot be condensation and thus inclusion of water between the clear lacquer and the base lacquer. Therefore even coatings which are soaked with solvent (for example water) are highly stable in respect of shearing and impact-resistant. An effect pigment which is treated in that way has accordingly become a 'chemical constituent' of the ambient medium.

The effect pigments according to the invention involve either metal pigments such as aluminium, copper, zinc, gold-bronze, titanium (EP 0 796 688), zirconium, tin, iron (EP 0 673 980) and steel pigments or pigments of alloys of the above-mentioned metals. The effect pigments can also comprise flake-form glass, $Al_2O$, $SiO_2$ (EP 0 803 550 A2), $TiO_2$ or mica. Multi-layer pigments (DE 44 05 492 A1, EP 0 708 154; DE 196 18 569) or pearl shine pigments or mixtures thereof can also be coated in accordance with the invention. The pigments may carry a coating of metal oxides such

as $SiO_2$ (for example: US No 2 885 366, US No 3 954 496, EP 0 678 561, DE 195 01 307, EP 0 708 155), $TiO_2$ (for example: 0 338 428), $Al_2O_3$ (for example: DE 195 20 312, EP 0 560 144) and $Fe_2O_3$ (for example: EP 0 033 457, EP 0 806 457) or organic polymers such as acrylate, methacrylate etc (for example: DE 40 30 727, EP 0 416 369). The particle size is between 1 and 200 µm.

The described demands on an orientation aid are satisfied in accordance with the invention by a bonding agent which carries two or more functional groups. One group of the bonding agent reacts with the surface of the effect pigment, which surface is possibly occupied by oxides. Alkoxysilyl groups (for example methoxy and ethoxy silanes), halosilanes (for example chlorosilanes) or acid groups of phosphoric acid esters or phosphonic acids and phosphonic acid esters are considered here. The described groups are linked by way of spacers of greater or lesser length to a second, preferably lacquer-friendly group. The spacer involves unreactive alkyl chains, siloxanes, polyethers, thioethers or urethanes or combinations of those groupings of the general formula $(C, Si)_nH_m(N,O,S)_x$ with n = 1 - 50, m = 2 - 100 and x = 0 - 50. The lacquer-friendly group preferably involves acrylates, methacrylates, vinyl compounds, amino or cyano groups, isocyanates, epoxy, carboxy or hydroxy groups. Upon baking or hardening of the coating those groups chemically react with the ambient medium in a cross-linking reaction in accordance with the known chemical reaction mechanisms.

The effect pigments according to the invention are produced by agitating and heating the initial pigments in an organic solvent, mixing with a solution of a base in water or another solvent, adding the surface-modifying agent, cooling after 15 minutes to 24 hours of reaction time, and suction removal. The filter cake obtained can be dried in a vacuum at about 60° - 130°C.

Silane-based surface-modifying agents are described for example in DE 40 11 044 C2. Phosphoric acid-based surface-modifying agents can be obtained inter alia as Lubrizol® 2061 and 2063 from LUBRIZOL (Langer & Co).

The surface-modifying agent can also be produced directly on the pigment by chemical reaction from suitable starting substances. In that case the effect pigments are also agitated and heated in an organic solvent. They are then mixed with the solution of a base. Preferably organic amines are used for the metal effect pigments which react with water, while predominantly mineral bases are used for the mineral effect pigments. There is then added a bonding agent which chemically reacts with the effect pigments and which is firmly bound to the pigment surface. That bonding agent is then reacted by way of a further functional group, possibly in the presence of an initiator (radical-forming agent, acids, bases etc) with a cross-linking agent, in which case however only a part of the functional groups of the cross-linking agent reacts with the bonding agent and another part remains free, that is to say it remains further capable of reaction. After about 1 - 6 hours of reaction time the pigment suspension is cooled and subjected to suction removal. The filter cake obtained in that way can be dried in a vacuum at 60° - 130°C.

The reaction can also be conducted in a solvent in which the coated effect pigments are later formed as a paste and used. That renders a drying step redundant. Specific examples of bonding agents that can be mentioned are for instance cross-linkable organo-functional silanes which after the hydrolysis operation are anchored with their reactive Si-OH units on the (partially oxidic) surface of the effect pigments. The potentially cross-linkable organic groups can later react with the lacquer binding agents. Examples of cross-linkable organo-functional silanes are as follows:

Vinyl trimethoxy silane, aminopropyl triethyoxy silane, N-ethylamino-N-propyl dimethoxy silane, isocyanatopropyl triethoxy silane, mercaptopropyl trimethoxy silane, vinyl triethoxy silane, vinyl ethyl dichlorosilane, vinyl methyl diacetoxy silane, vinyl methoyl dichlorosilane, vinyl methyl diethoxy silane, vinyl triacetoxy silane, vinyl trichlorosilane, phenyl vinyl diethoxy silane, phenyl allyl dichlorosilane, 3-isocyanatopropoxyl triethoxy silane, methacryloxy propenyl trimethoxy silane, 3-methacryloxy propyl trimethoxy silane, 3-glycidyloxypropyl trimethoxy silane, 1,2-epoxy-4-(ethyl triethoxysilyl)-cyclohexane, 3-acryloxypropyl trimethoxy silane, 2-methacryl-oxyethyl trimethoxy silane,

2-acryloxyethyl trimethoxy silane, 3-methacryloxypropyl triethoxy silane, 3-acryloxypropyl trimethoxy silane, 2-methacryloxyethyl triethoxy silane, 2-acryloxyethyl triethoxy silane, 3-methacryloxypropyl tris(methoxyethoxy)silane, 3-methacryloxypropyl tris(butoxyethoxy)silane, 3-methacryloxypropyl tris(propoxy)silane, 3-methacryloxypropyl tris(butoxy)silane, 3-acryloxypropyl tris(methoxyethoxy)silane, 3-acryloxypropyl tris(butoxyethoxy)silane, 3-acryloxypropyl tris(propoxy)silane, 3-acryloxypropyl tris(butoxy)silane. 3-Methacryloxypropyl trimethoxy silane is particularly preferred.

These and other silanes are commercially available for example from ABCR GmbH & Co, D-76151 Karlsruhe, or Sivento Chemie GmbH, D-40468 Düsseldorf.

Vinyl phosphonic acid or vinyl phosphonic acid diethyl ester can also be listed here as bonding agents (manufacturer: Hoechst AG, Frankfurt am Main).

If acrylate/methacrylate silanes are used as bonding agents, it is possible to use the following multi-functional acrylates or methacrylates as cross-linking agents:

Tetraethylene glycol diacrylate (TTEGDA), triethylene glycol diacrylate (TIEGDA), polyethylene glycol-400-diacrylate (PEG400DA), 2,2'-bis(4-acryloxyethoxyphenyl)propane, ethylene glycol dimethacrylate (EGDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TRGDMA), tetraethylene glycol dimethacrylate (TEGDMA), butane-1,3-diol dimethacrylate (1,3-BDDMA), butane-1,4-diol dimethacrylate (1,4-BDDMA), hexane-1,6-diol dimethacrylate (1,6-HDMA), dodecane-1,12-diol dimethacrylate (1,12-DDDMA), neopentyl glycol dimethacrylate (NPGDMA), trimethylol propane trimethacrylate (TMPTMA) and hexane-1,6-diol diacrylate (1,6-HDDA). Trimethylol propane trimethacrylate (TMPTMA) is particularly preferred.

When using epoxy silanes as bonding agents for example it is possible to use the following multi-functional amines as cross-linking agents: 3,3-dimethyl-4,4-diaminodicyclohexyl methane, ethylene diamine, triethylene tetramine, meta-xylylene diamine, N-aminoethyl piperazine, 2-

methyl-1,5-pentamethylene diamine, 1,2-diaminocyclohexane and isophorone diamine.

If amino silanes are used as bonding agents it is possible to use for example the following multi-functional epoxy compounds as cross-linking agents: butane-1,4-diol diglycidyl ether, glycerine triglycidether, neopentylglycol diglycidyl ether, pentaerythritol polyglycidether, hexane-1,6-diol diglycidether, polypropylene glycol diglycidyl ether and trimethylol propane triglycidether.

The specified acrylates and methacrylates can be obtained for example from Elf Atochem, D-40401 Düsseldorf, Röhm, Darmstadt and Servo, 7490 AA Delden (Netherlands). All the mentioned multi-functional amine and epoxy compounds are commercially available, thus for example from UPPC, D-88487 Mietringen-Baltringen.

Commercially available organic peroxides but also inorganic peroxides and diazo compounds can be used as thermal initiators. Examples of such peroxides are diacetyl peroxides such as acetyl-cyclohexane-sulphonyl peroxide, bis(2,4-dichlorobenzoyl) peroxide, diisononanoyl peroxide, dioctanoyl peroxide, diacetyl peroxide and dibenzoyl peroxide; peroxydicarbonates (for example diisopropyl peroxydicarbonate, di-n-butylperoxydicarbonate, di-2-ethylhexyl-peroxydicarbonate, dicyclohexyl-peroxydicarbonate), alkyl peresters (for example cumyl perneodecanoate, t-butyl-perneodecanoate, t-amyl-perpivalate, t-butyl-per-2-ethylhexanoate, t-butyl-perisobutyrate, t-butyl perbenzoate), dialkyl peroxides (for example dicumyl peroxide, t-butylcumyl peroxide, 2,5-dimethylhexane-2,5-di-t-butyl peroxide, di(t-butylperoxyisopropyl)benzene, di-t-butylperoxide or 2,5-dimethylhexine-3-2,5-di-t-butyl peroxide), perketals (for example 1,1'-bis(t-butylperoxy)-3,3,5-trimethylcyclohexanone peroxide, methylisobutyl ketone peroxide, methyl ethyl ketone peroxide or acetyl acetone peroxide), alkyl hydroperoxides (for example pinane hydroperoxide, cumol hydroperoxide, 2,5-dimethyl hexane-2,5-dihydroperoxide or t-butylhydroperoxide), azo compounds (for example 4,4'-azo-bis(4-cyanovaleric acid), 1,1'-azo-bis(cyclohexane carboxylic acid nitrile), 2,2'-azo-bis(isobutyric acid amidine) dihydrochloride, 2,2'-azo-bis(isobutyric acid nitrile)) or

persulphates such as sodium peroxydisulphate and potassium peroxodisulphate. Particularly preferred is 2,2'-azo-bis(isobutyric acid nitrile).

The specified compounds are commercially available from Aldrich Chemie, D-89552 Steinheim.

The sectors of use of the described invention are primarily aqueous paints and lacquers and printing inks. Here the described process provides for a brilliant shiny appearance of the effect pigments with at the same time good adhesion (cross-cutting test, Tesa test) and mechanical stability (stone impact test). The good adhesion of the coating is maintained even under the action of aggressive and corrosive media such as condensed water (for example the condensed water test in accordance with DIN 50 017). Even in powder lacquers and plastic materials the invention improves the bond of the pigments to the ambient medium and thus the mechanical and chemical properties of the coating system.

In accordance with the invention it is also possible to provide on the initial pigment a layer which includes side by side one or more of the above-mentioned hydrophobing alkyl silanes (for example described in EP 0 634 459 A2) and at least one of the reactive orientation aids described herein. Depending on the specific demands made on the pigment, the proportion of the surface-modifying agent described herein in that layer can basically be between 10% and 100%. It is particularly preferred however if the proportion is 10, 30, 50, 75 or 100%, as that provides for graduation of the operative bonding forces, such as to do justice to the most frequently occurring demands in a practical context. That provides for both improved orientation of the pigments in the lacquer, which is greater in accordance with the content of reactive orientation aids, and also strengthened binding in the hardened film of lacquer.

It is to be mentioned in general terms that the aluminium pigments according to the invention which are coated with a layer comprising a reactive surface-modifying agent can be dispersed markedly more easily than for example chromated aluminium types (for example Hydrolux types, Eckart-Werke). The dispersion of Al-pigments is a critical step as the Al-flakes can be mechanically damaged by the application of high levels of

shearing energy. Lacquer films with such damaged pigments exhibit an unwanted 'greyed' appearance (the metallic shine of such coatings is markedly reduced).

Paints and printing inks which contain pigments in flake form cause problems in terms of handling insofar as, because of their size and density in comparison with the medium surrounding them, the pigments can easily settle and then cake together to form a solid sediment cake. That applies primarily in regard to mineral and oxidic effect pigments. The pigments according to the invention described herein do not settle in a lacquer so easily as a bottom sediment in comparison with the non-coated initial material, or after sedimentation they can be re-dispersed again markedly more easily.

Surface-modified flake pigments with improved settlement and sediment-agitation characteristics have already been described. EP 0 515 928 refers to coating pigments with a polyacrylate or polymethacrylate or salts thereof. There is no disclosure of more detailed information regarding the polyacrylates used so that the structural configuration of the coating is also unknown. This coating also does not contribute to improving orientation and thus the optical properties of the pigments; this coating also cannot make any contribution to controlling the wetting characteristics or improved adhesion.

EP 0 523 357 describes flake substrates which are coated with a modifying reagent comprising binding agent and particles in fibre form, to improve the settlement and sediment-agitation characteristics. The fibres prevent the coated substrates resting on each other by virtue of steric repulsion and thus being able to entail strong adhesion to each other. The fibres however are not/do not become chemically firmly anchored on the pigment surface or in the binding agent medium so that the fibres can become detached and can adversely influence the rheology of the lacquer or the printing ink.

PCT WO 96/32446 describes various compounds having epoxy groups, which together are intended to improve the settlement characteristics and also the weathering of pigments in flake form. As only similar reactive groups are present, a specifically targeted and oriented

construction of a reactive orientation aid on the pigment surface is not possible.

Passivated Al-pigments for use in aqueous base lacquers (EP 0 259 592) are produced inter alia in the form of aqueous pigment pastes. Stability in terms of storage of such pastes which are produced in accordance with EP 0 259 592 is severely limited in terms of time as, in spite of passivation, the highly exothermic reaction of water with aluminium, with the formation of hydrogen, cannot be entirely stopped. The described modified new types of pigment on an aluminium basis have markedly prolonged stability in terms of storage, in comparison with passivated chromated aluminium types (Hydrolux types, Eckart-Werke).

Table 1 compares the properties in terms of use of various coated aluminium pigments (fineness $D_{50}$ = 18 - 20 µm in a commercially available aqueous lacquer system. It can be clearly seen that the $SiO_2$-coated pigment quality V2521 which is surface-modified with the described bonding agents at least achieves and in part even exceeds the properties profile of commercially available chromated types (Hydrolux 8154, Eckart-Werke). Type V2421 involves $SiO_2$-coated pigments which are modified with alkyl silanes while PCR 8154 (Eckart-Werke) which is available on the market is coated with pure $SiO_2$.

Table 1:

ME-values, condensed water test and stone impact test on coated aluminium pigments.

Layer structure: phosphated steel sheet, KTL, filler, commercially available water-based lacquer on a polyurethane/polyacrylate base, 1K-High-Solid clear lacquer.

| Type[1] | ME-value[2] | Cross-cutting test Gtc[3] | Stone impact test[4] |
|---|---|---|---|
| PCR 8154 | 284 | - | - |
| Hydrolux 8154 | 400 | + | + |
| V2421 | 414 | - | - |
| V2521 | 383 | +/++ | +/++ |

- = inadequate

+ = good

++ = very good

[1] Detailed description in the text

[2] Measurement with goniophotometer GP 3 (Zeiss), typical values.

[3] Checking immediately after the condensed water test in accordance with DIN 50 017.

[4] 450g of steel balls (Ø 3 - 5 mm) are accelerated under free fall in a vertical tube (6m in length) and impinge at the end of the tube on the sheet which is lacquered as described.

Example 1:

100g of coated aluminium pigment (for example PCR 8154, Eckart-Werke) is agitated in 500 ml of ethanol for 10 minutes. The suspension is heated with agitation to 80°C and mixed with a solution of 2.34g of triethylamine in 26 ml of water. After a further 5 minutes 1g of 3-methacryloxypropyl trimethoxy silane is added to the mixture. 30 minutes later 2g of trimethylolpropane trimethacrylate is added to the mixture, followed immediately by 30 mg of α, α'-azo-isobutyronitrile. The entire mixture is stirred for a further period of 4 hours at 80°C. The mixture is then allowed to cool down and the finished-coated pigment is subjected to suction removal. Finally the filter cake is dried at 90°C in a vacuum.

The pigment powder is applied in a commercially available aqueous binding agent system. The freshly lacquered test sheet is pre-dried at 80°C in a drying cabinet (10 minutes). The clear lacquer is then applied and the finished coating is baked at 130°C (30 minutes).

Example 2:

100g of coated aluminium pigment is modified as described in Example 1. Instead of 2.34g of triethylamine 1.17g of ethylene diamine is used.

Example 3:

100g of a commercially available pearl shine pigment (for example Flonac MI 11, Eckart-Werke) is modified as described in Example 1. 26 ml of 1 N KOH is used as the base.

Example 4:

100g of coated aluminium pigment is modified as described in Example 1. Instead of 1g of 3-methacryloxypropyl trimethoxy silane 1g of vinyl trimethoxy silane is used.

Example 5:

100g of oxidised aluminium pigment (for example in accordance with PCT/DE96/00890) is agitated in 500 ml of ethanol for 10 minutes. The suspension is heated with agitation to 80°C and mixed with a solution of 2.34g of triethylamine in 26 ml of water. After a further 5 minutes 2g of urethane methacrylate alkoxy silane (H Wolter et al, Polymer & Materials Research Symposium 1993, Bayreuth, pages 14 - 17) is added to the mixture. 30 minutes later 2g of trimethylol propane trimethacrylate is added to the mixture, followed immediately by 50 mg of α; α'-azo-isobutyronitrile. The entire mixture is agitated for a further 6 hours at 80°C. The mixture is then allowed to cool down and the finished-coated pigment is subjected to suction removal. Finally the filter cake is dried at 90°C in a vacuum.

The pigment powder is applied in a commercially available aqueous binding agent system. The freshly lacquered test sheet is pre-dried at 80°C in a drying cabinet (10 minutes). Then the clear lacquer is applied and the finished coating baked at 130°C (30 minutes).

Example 6:

As Example 5, but instead of urethane methacrylate alkoxy silane and trimethylol propane trimethacrylate (see Example 5) 3g of the adduct of 3-mercaptopropyl trimethyoxy silane to trimethylol propane

trimethacrylate (H Wolter et al, Mat. Res. Soc. Symp. Proc. Vol 271, page 719, 1992) is used.

Example 7:

As Example 6, but using a commercially available trialkoxysilyl-substituted polyethylene imine.

Example 8:

As Example 6 but with the addition of a commercially available polyethylene/acrylic acid copolymer.

Example 9:

As Example 1 but using a mixture comprising 1g of 3-methacryloxypropyl trimethoxy silane and 1g of hexadecyl trimethoxy silane instead of 3-methacryloxypropyl trimethoxy silane and trimethylol propane trimethacrylate.

Example 10:

As Example 1, but using 100g of a commercially available pearl shine pigment (for example Flonac MI 11, Eckart-Werke).

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Effect pigment coated with surface-modifying agents, characterised in that the initial pigment has a layer with at least one reactive surface-modifying agent, wherein the surface-modifying agent is a compound which has at least two terminal functional groups which are different from each other and which are spaced by a spacer comprising alkyl chains, silanes, siloxanes, polyethers, thioethers or urethanes or combinations of those groupings having the general formula $(C,Si)_nH_m(N,O,S)_x$ with n = 0-50, m = 0-100 and x = 0-50, and of which at least one functional group is chemically bound to the initial pigment, and the effect pigment is further of a particle size of between 1 and 200 µm and exhibits the behaviour of a non-leafing pigment.

2. An effect pigment according to claim 1 characterised in that the surface-modifying agent is in monomeric or polymeric form.

3. An effect pigment according to claim 1 or claim 2 characterised in that the surface-modifying agent is chemically bound to the initial pigment by way of a reaction of the at least one functional group comprising $(RO)_3Si$-, $(RO)_2RSi$-, $R_{(3-z)}X_2Si$-, $O=P(OR)_x(OH)_y$-$O_w$-, wherein within a functional group R can be the same or different and respectively represents $C_nH_m$, wherein n = 1-30, m = 3-61, z = 1-3 and wherein X = Cl, Br and x = 0-2, y = 0-2 and x + y = 2 .and w = 0 or 1.

4. An effect pigment according to any one of claims 1 to 3 characterised in that at least one further functional group present involves an acrylate, methacrylate, isocyanate, a vinyl compound, amino group, cyano group, epoxy group or hydroxy group.

5. An effect pigment according to any one of claims 1 to 4 characterised in that the effect pigment is selected from the group consisting of aluminium, copper, zinc, gold-bronze, titanium, zirconium, tin, iron, steel and/or alloys thereof, glass, $Al_2O_3$, $SiO_2$, $TiO_2$ or mica or multi-layer pigments or pearl shine pigments or mixtures thereof.

6. An effect pigment according to any one of claims 1 to 5 characterised in that the effect pigment is coated with a layer comprising one or more metal oxides from the group consisting of silicon dioxide, titanium dioxide, aluminium dioxide, tin oxide, zinc oxide, iron oxide and/or organic polymers.

7. An effect pigment according to claim 6 wherein the organic polymers are selected from acrylates and/or methacrylates.

8. An effect pigment according to any one of the preceding claims characterised in that besides the reactive surface-modifying agent an alkyl silane is present in the same layer.

9. An effect pigment according to any one of the preceding claims characterised in that the reactive surface-modifying agent is contained in the layer in a proportion of between 10 and 100%, wherein the remaining 0 to 90% are comprised of one or more of hydrophobing alkyl silanes.

10. An effect pigment according to claim 9, wherein the reactive surface-modifying agent is contained in the layer in proportions of 10, 30, 50, 75 or 100%.

11. A process for the production of an effect pigment according to any one of the preceding claims characterised in that the initial pigment is heated, mixed with a solution of a base in water or in another solvent, the surface modifying agent is added and after 15 minutes to 24 hours cooling is effected followed by suction removal and the filter cake obtained is then dried at between about 60 and 130°C in a vacuum.

12. A process for the production of an effect pigment according to any one of claims 1 to 10 characterised in that the surface-modifying agent is produced directly on the surface of the initial pigment by chemical reaction from suitable components.

13. Use of an effect pigment coated with orientation aids according to any one of claims 1 to 10 for the production of paints, printing inks, lacquers, coatings and plastic materials, for colouring ceramics and in cosmetic preparations and writing, painting and drawing pencils and crayon

Dated this 28th day of March 2002

Eckart-Werke Standard Bronzepulver-Werke Carl Eckart GmbH & Co.,
Patent Attorneys for the Applicant:

F B RICE & CO